JOURNAL OF CATALYSIS **176,** 561–568 (1998)
ARTICLE NO. CA982079

SIMS/XPS Study on the Deactivation and Reactivation of B-MFI Catalysts Used in the Vapour-Phase Beckmann Rearrangement

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Received January 5, 1998; revised March 16, 1998; accepted March 16, 1998

A weakly acidic borosilicate of MFI-type (B-MFI) was utilized as a catalyst for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in a vapour phase process. XPS and SIMS depth profiling techniques were applied to study the fresh catalyst as well as the deactivation and the reactivation phenomena on and below the catalyst surface. The catalyst deactivation could not be attributed to excessive amounts of carbon deposited on the surface or to a pronounced and irreversible deboration of the zeolite. A pore blocking effect caused by an enrichment of nitrogen-containing species inside the pore system was observed. These species were presumably formed by ring-opening reactions of unsaturated nitriles preferentially formed inside of the zeolite. Furthermore, distinct changes of the $SiO^+/SiOH^+$ fragment ion profiles in the surface near regions of the pore system were observed but the $SiO^+/SiOH^+$ fragment ion ratios in the topmost atomic layers of the fresh and the reactivated catalyst were nearly identical. This indicates that the level of SiOH-groups at the catalyst surface, which are active sites for the given process, was retained or reestablished during the whole time of catalyst service and the regeneration, whereas the silanol group density in the pore system below the surface was tremendously affected. Indications were obtained that Na is located at lattice sites, whereas Ca is able to diffuse inside the pore system of the B-MFI catalyst.

INTRODUCTION

The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam as a starting material for the synthesis of nylon 6 is catalyzed by highly concentrated sulfuric acid in a homogeneous liquid phase process (1). Under these conditions corrosion problems arise as well as waste deposal costs due to the simultaneous production of high amounts of ammonium sulfate ranging from about 2.5 up to 4 t sulfate per 1 t of lactam.

Therefore, new experimental work is focused on utilizing heterogeneous catalysts for conducting the rearrangement reaction in a vapour-phase process. The benefits of catalytic centres of moderate acidity such as on ZSM5 with low Al-content for the given process were highlighted in (2–7). The weakly acidic borosilicate of the MFI-type (B-MFI, formerly boron pentasil zeolite) is very suitable for the Beckmann rearrangement, too. The activity of B-MFI catalysts in fixed bed and fluidized bed reactors and the deactivation and reactivation has been studied in detail (8–10).

Complementary to the catalyst testing the changes at the catalyst surfaces themselves and the catalytic features were monitored by means of surface spectroscopic techniques. In the present paper, the results of X-ray photoelectron spectrometry (XPS) and secondary ion mass spectrometry (SIMS) on the changes in the surface and near-surface regions of the B-MFI catalysts are reported.

It is shown that, even in the depth-profiling mode, these techniques are very suitable for investigating the changes of this porous, nonconducting zeolite material during catalyst operation and reactivation.

EXPERIMENTAL

Catalysts

B-MFI samples were measured in the following conditions:

—Original, fresh catalyst.

—After use in the vapour-phase Beckmann rearrangement carried out in an integral fixed bed reactor at increasing serving time of the B-MFI catalyst; catalyst activities: 98%, 50%, and 30%, respectively (8).

—After regeneration of a deactivated catalyst in air at $T = 500°C$.

Additional details on the catalyst preparation and test conditions, as well as the catalytic performance and the regeneration were reported in (8–10). The crystallite size of the spherical-shaped particles was below 1 μm (8–10). ICP (inductive coupled plasma) analysis revealed typical bulk compositions of 339.5 mg/g of silicon, 8.67 mg/g of boron, and 0.54 mg/g of sodium. Calcium and potassium, which were

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0021-9517/98 $25.00

detected by means of SIMS (*v.i.*, Fig. 7), and aluminium were below the dection range of ICP. Na, K, and Ca are residual contaminations originating from the synthesis process and the starting materials.

The catalyst pellets were subjected to the surface spectroscopical investigations without any further pretreatment.

SIMS/XPS Measurements

The use of sputter techniques for revealing and comparing the properties in the topmost atomic layers and the selvedge regions of materials is well established (11, and literature cited therein). Sputter depth-profiling measurements are not confined to analyzing flat, homogeneous and well-defined surfaces. Since the energy of the primary ions is dissipated in a collision cascade into the target material (12), a rigid geometrical arrangement between the incident beam and a flat target surface is not essential. Events such as recoil sputtering in a fixed centre of mass frame are not of predominant importance to obtain adequate data from rough or porous surfaces. SIMS in-depth fragmentation profiles can be quite helpful in studying finely disperse, powdered materials as well. This was shown (e.g.) by the work of Dwyer *et al.* on the framework substitution in iron molecular sieves (13). Furthermore, a SIMS study on the C/H fragmentation patterns of the surface and selvedge regions of activated carbons and of carbon blacks (fluffy and pelletized) before and after controlled oxydation was presented in (14, 15).

In the present work an attempt is made to elucidate the potential of SIMS experiments on the given porous, nonconducting zeolite material. Since even in the static SIMS mode the amount of reference data on the secondary ion yields and the matrix effects in oxidic catalyst systems is still limited, e.g. (16–18 and literature cited therein) a strictly consistent quantitative evaluation of sputter-depth profiles of the B-MFI material is not straightforward. At the present state it still seems necessary to discuss the results from in-depth analyses of porous oxidic materials by means of SIMS in terms of fragmentation profiles rather than to directly reflect the quantitative concentration profiles of the elements. Therefore, the SIMS investigations were assisted by complementary XPS measurements to obtain corresponding quantitative, or, after sputtering, roughly semiquantitative data on the composition.

SIMS in-depth fragmentation profiles were recorded using 5 keV Ar^+ ions at 0.3 μA in the spectra acquisition (gated mode) and 3.0 μA for the surface erosion sequences. A Leybold IQ12/38 ion gun was used. The spot size was 6 mm $\times$ 6 mm. Charge compensation was performed by an optimized low energy electron flood-gun. The stability of the ion beam current, the size of the beam and the beam profile was repeatedly monitored by means of a Faraday cup/ion collector device and a picoamperemeter as well as by sputter experiments on tantalum oxide specimens (NPL/BCR reference material S8F88A,). A QMG 512 quadrupole mass spectrometer (Balzers) was utilized for the detection of the secondary ions.

The XPS measurements were performed using MgK_α radiation at a power of 150 W. The electron energy analyzer (Leybold EA200) was operated at a pass-energy of 72 eV in the fixed analyzer transmission mode. The binding energy scale of the spectrometer was referenced to the $Au4f_{7/2}$ signal of the SCAA83 standard of the National Physics Laboratory (NPL, Teddington, UK) at 84.0 eV (19) which was measured before and after studying the catalysts. The electrostatic charging of the catalyst pellets was compensated by low energy electrons from a controlled glow emission source, operated in the vicinity of the sample holder. The emission source was shielded and thermally insulated to prevent any direct heat transfer to a catalyst sample. Control experiments were performed by separately changing the electrostatic potential at the entrance aperture of the electron analyzer to exclude artefacts due to homogeneous or inhomogeneous electrostatic charging such as line broadening and line shape deformation. For recording XPS depth profiles a Wien-filtered 5 keV Ar^+ beam from a Leybold gun (IQ 12/38) was operated at 3 μA onto 6 mm $\times$ 6 mm spot-size. The use of a small-spot XPS lens system (Leybold) and optical microscopy allowed to focus the XPS analysis into the inner 80% of the centre region of the eroded catalyst surface. A DS100 data set was utilized to evaluate the XPS data with standard routines (subtraction of X-ray satellites, Shirley-type background subtraction, correction by relative sensitivity factors).

The reproducibility of the SIMS and XPS depth profiles obtained was checked several times on separate specimens of a given catalyst sample. The erosion conditions were kept constant during the whole set of XPS and SIMS experiments.

Sample Preparation

The zeolite particles were arranged in gold-coated stainless steel vessels without compressing, glueing, or any other additional treatment to avoid any external contamination. Separate samples of a single lot were prepared and used for the XPS and the SIMS measurements, respectively.

Each sample was introduced separately into a differentially pumped prechamber of the XPS and the SIMS spectrometer systems and was pumped down to 10^{-8} mbar. Afterwards, the sample was transferred into the main chamber of the XPS and the SIMS spectrometer. The purity of the vacuum of the spectrometer system with a base pressure of 4×10^{-10} mbar was continuously monitored by means of residual gas mass spectrometers (Quadrex 200, Inficon) to exclude artefacts due to adventitious hydrocarbons and cross-contaminations.

In between the SIMS measurements a gold target (99.999%, Demetron) was repeatedly sputtered with Ar$^+$-ions to exclude memory effects due to sputtered oxide material around the entrance aperture of the ion optical system of the SIMS-quadrupole system.

Continuous observations by means of optical microscopy confirmed that the optimized charge compensation techniques were suitable to protect the loose particles of the material from mechanical movements due to electrostatic spraying during the ion bombardment. This was strictly controlled for the case of each single sample.

RESULTS AND DISCUSSION

Figure 1 depicts the SIMS depth profiles of the B-MFI catalysts investigated at various activity levels. The in-depth variations of the secondary ion intensities of boron, silicon, carbon, and oxygen are compared for a fresh, a deactivated, and a regenerated B-MFI catalyst. For the fresh catalyst no significant changes of the Si and B signals as a function of depth occur, whereas the deactivated specimen shows lower intensities of Si and B in the surface regions due to the deposition of carbon. The carbon is indicated by increased

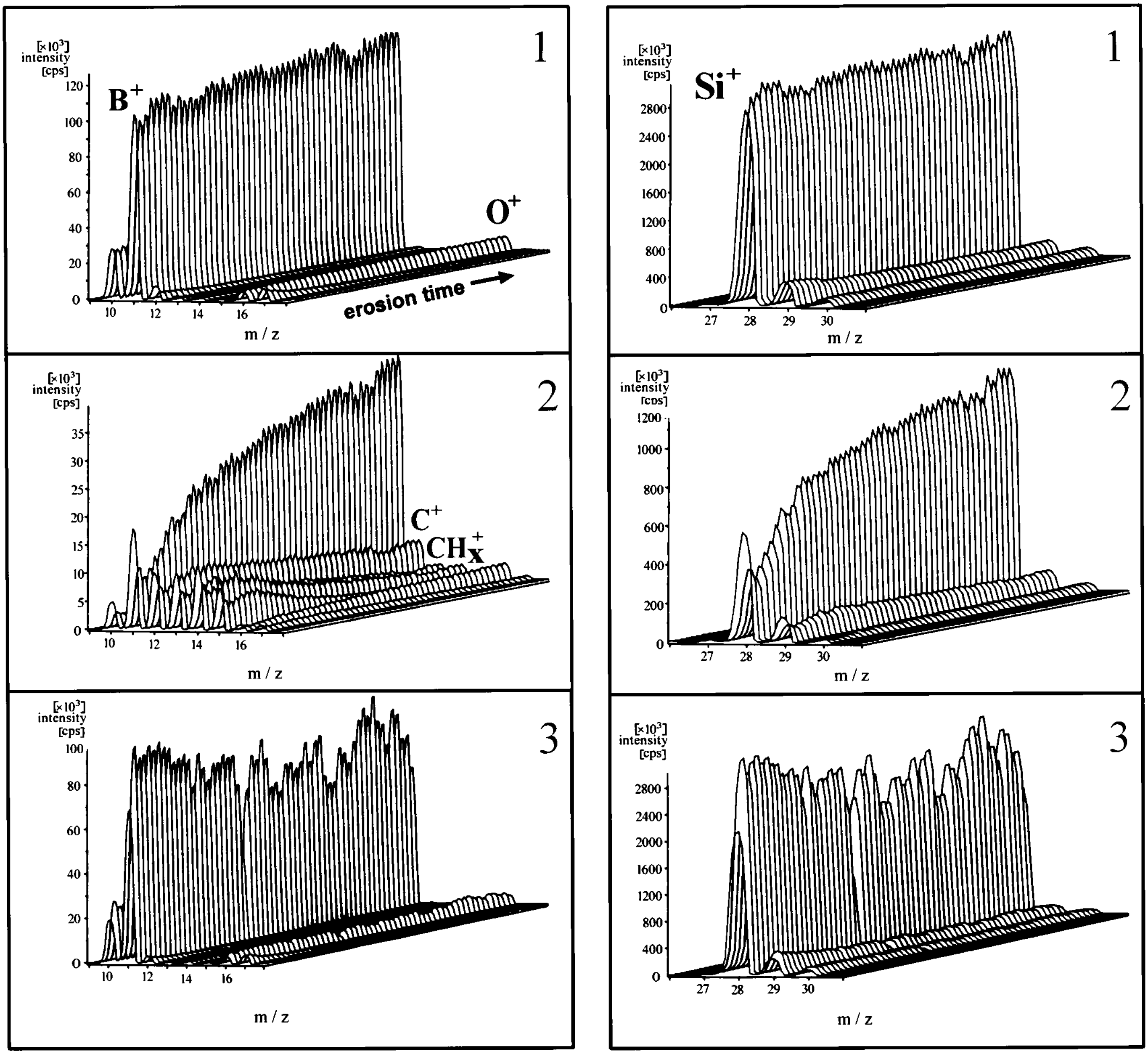

FIG. 1. SIMS depth profiles of B-MFI catalysts: left, B$^+$ (10, 11), C$^+$, CH$_x^+$ (12, 13, 14), and O$^+$/OH$^+$ (16, 17)-region; right, Si$^+$-signal region (28, 29, 30). 1, fresh catalyst; 2, used catalyst after deactivation, residual activity 30%; 3, used catalyst after oxydative regeneration.

TABLE 1

Results of a Quantitative Evaluation of XPS-Spectra as Measured Before (Surface) and After (Subsurface) Ar^+-Ion Bombardment of B-MFI Catalysts of Different Catalytic Activity

Surface	Original	30% activity	After regeneration
O	59	44	59
N	—	1.3	—
C	1.0	16	5.7
B	1.9	traces	1.6
Si	37	39	34
Subsurface			
O	58	52	60
N	—	0.8	—
C	0.7	5.2	—
B	1.8	0.4	3.0
Si	39	42	37

Note. Relative sensitivity factors: O 1s: 0.61, N 1s: 0.36, C 1s: 0.20, B 1s: 0.101, Si 2p: 0.195.

relative intensities of C^+, CH^+, CH_2^+, CH_3^+. The corresponding XPS data showed that the C 1s signals appeared at binding energies between 284.8–285.1 eV which is an indication for aliphatic carbon (20, 21) and not for coke-like deposits or carbons of enhanced aromaticity or sp^2-character (20–24). The concentrations of the elements as determined by means of XPS in a separate set of XPS depth profiling experiments are given in Table 1. With respect to preferential sputtering effects the XPS data obtained after surface erosion are given for a qualitative comparison of the active, deactivated, and reactivated material, respectively. The results of the quantitative evaluations are given in percentage of area. It is surprising that even in the sample having 30% activity left, only about 16% of the carbon is present on the catalyst surface. The high carbon level to be expected for an (e.g.) coked catalyst is not observed.

The initially enhanced intensity of the B and Si signals in the first spectra of the deactivated catalyst (Fig. 1, Section 2) may be due to the influence of OH-groups and traces of adsorbed water on the relative secondary ion yields of these elements in the topmost atomic layer. This was not the case in the corresponding XPS depth profiles. This observation may partly explain why different B/Si values were obtained by evaluating the XPS data (Table 1), on the one hand, and the qualitative comparison of the SIMS fragment ion ratios of Si and B (Table 2), on the other.

Compared to the sufficiently smooth Si and B profiles of the fresh catalyst the SIMS-profiles of the regenerated material show some discontinuities (Fig. 1, Section 3). This cannot be attributed to instabilities of the primary ion beam. It may be caused by incomplete charge compensation inside the zeolite lattice during the SIMS experiment. This usually appears in the case of dried material having comparatively low amounts of carbon and of hydroxyl groups or adsorbed water species. This interpretation is supported by the SIMS profiles in Fig. 2. It is evident that the $SiO^+/SiOH^+$ fragment ion ratio changes significantly in the near-surface regions with increasing service time of the catalyst. With respect to the SiO^+ signal the reactivated catalyst shows the steepest profile of the $SiOH^+$ cluster ion signal as a function of depth. The changing surface conditions of the catalyst influence the secondary ion yields. Therefore, it is not justified to compare directly the intensity scales of the spectra but a qualitative comparison of selected fragment ion ratios appears to be straightforward. Fragment ion ratios from the first and the last SIMS spectrum of a depth profile are given in Table 2. It is remarkable that the $SiO^+/SiOH^+$ fragment ion ratios in the fresh and the regenerated condition are largely constant (0,41/0,38, Table 2). It follows that the silanol group density in the topmost atomic layers which is responsible for the catalytic activity is not irreversibly changed. The gradients of the $SiOH^+$ fragmentation profiles in the near-surface regions of the fresh and the reactivated catalyst are slightly different, whereas the gradients of the $SiO^+/SiOH^+$ profiles during catalyst operation are tremendously affected (Fig. 2).

Typical results on the carbon distribution from corresponding XPS depth profiles are compared in Fig. 3. The profile of the C-traces in the fresh material gives a rough impression of the low but rather constant carbon background level on and inside the porous zeolite material. (*N.b.*, the intensity scale for the XPS spectra of the fresh catalyst is enhanced.)

Similar to the SIMS profile shown in Fig. 1 the C 1s photoelectron signal of the carbon deposits on and in the deactivated catalyst decreases slowly with increasing material erosion time. A small line asymmetry of the C 1s signal in the topmost layers may be due to traces of adsorbed degradation products such as cyanopentene and cyclohexanone which were also detected by means of chromatographic methods.

On the other hand, a very steep C-gradient is observed for the catalyst after regeneration (Fig. 3, Section 3). Only a fraction of the topmost atomic layer of the outer surface of the zeolite is partly covered with adsorbed C-species,

TABLE 2

Comparison of Selected SIMS-Fragment Ion Ratios as Derived from the First (S) and the Last (E) Spectrum of In-depth Profiling Measurements

	Si^+/B^+		$SiO^+/SiOH^+$		B^+/C^+	
	S	E	S	E	S	E
Unused reference	26,3	24,8	0,41	6,08	13,0	93,9
98% activity	29,0	26,3	0,37	3,10	2,45	17,5
50% activity	29,9	27,7	0,33	2,53	1,83	8,52
30% activity	31,6	29,2	0,21	2,34	1,78	5,75
After regeneration	31,0	30,8	0,38	9,34	20,2	170

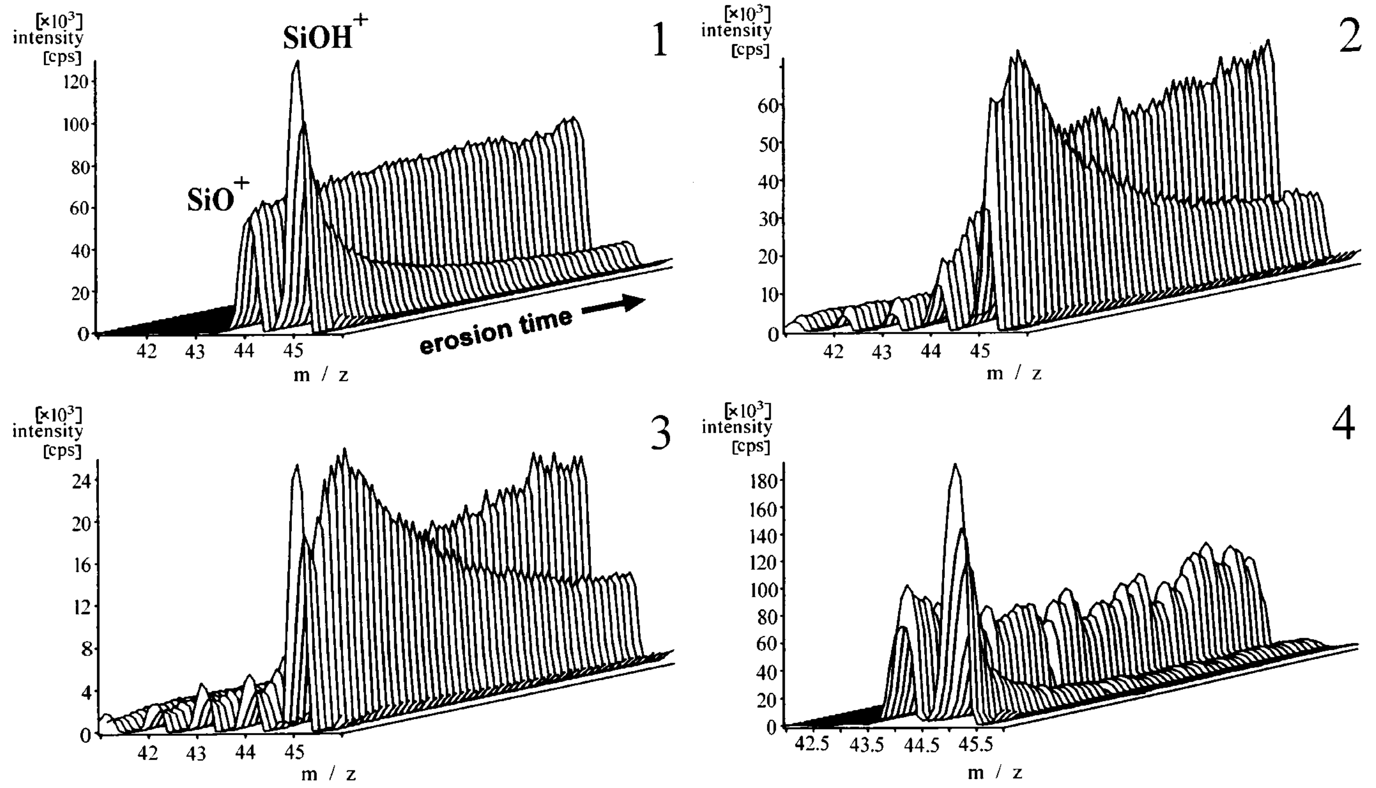

FIG. 2. SIMS depth profiles of B-MFI catalysts: SiO^+ and $SiOH^+$ signals (44, 45). 1, fresh catalyst; 2, used catalyst, 98% activity; 3, used catalyst, 30% activity; 4, used catalyst after oxydative regeneration.

predominantly aliphatic carbon (285 eV), some heterofunctional groups (286–287 eV), and traces of carbonates (289–290 eV) (20, 22). In this case carbon can be regarded as a pure surface contamination due to readsorption at the outer surface of the catalyst exclusively. The carbon content inside the pore system of the zeolite is below the XPS detection limit and is lower than the C-level of the fresh material (Table 1).

The XPS depth profile of the B-MFI catalyst having 50% activity left (Fig. 4) shows, that nitrogen had penetrated into the material as well. Comparing the N 1s binding energy values with reference data (20, 25) indicates that in the topmost atomic layers partly oxidized species of nitrogen appear at about 402–405 eV and aminofunctional and ammonium-like species in the near-surface regions at around 399–400 eV. In addition, Fig. 5 shows that, surprisingly, the concentration gradients of C and N are contrary, indicating a surface enrichment of carbon in the outermost layers but an enrichment of nitrogen inside the zeolite lattice. This was observed for all of the catalyst specimens used. This might be a hint that in the zeolitic channels linear N-containing compounds such as hexene nitriles are formed and subsequently oligomerized or polymerized, resulting in the blockage of pores. However, a final conclusion about the nature of the nitrogen-containing species only on the basis of the N 1s-binding energy values measured is not possible, since an influence of the sputtering procedure on the binding energy values obtained after surface erosion cannot be ruled out.

Contrary to the rather constant SIMS intensity profiles of Si and B profiles (see Fig. 1) Fig. 6 illustrates that the signal intensity of Na increases with increasing depth. The same shape of the Na profile was observed nearly perfectly for all the other catalyst samples from the different steps of catalyst deactivation and reactivation. On the other hand, the relative intensity of the Ca signal showed a pronounced decrease relative to the Si, Na, or K signals with increasing time of use. This is shown in Fig. 7. On the other hand, the shapes, but not the relative intensities of the K and Ca profiles of the reactivated material were quite similar to the fresh specimen.

CONCLUSIONS

The deactivation effects on the B-MFI catalysts during use in the Beckmann rearrangement reaction cannot simply be attributed to a pronounced surface-blocking due to an enhanced deposition of carbons such as coke or degradation products at the catalyst surface. Only about 16% of the surface area of the most deactivated specimen was

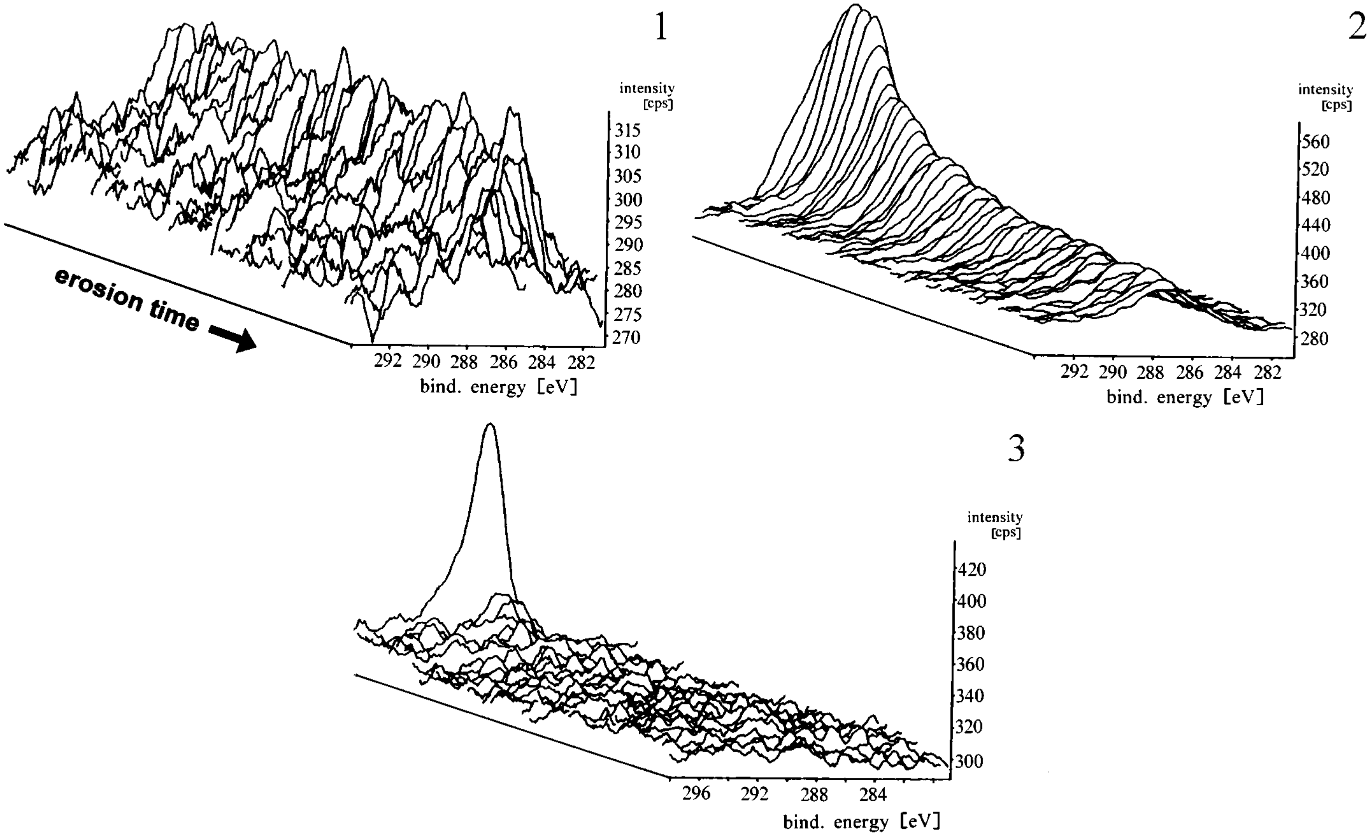

FIG. 3. XPS depth profiles of B-MFI catalysts: C 1s signal region. 1, fresh catalyst; 2, used catalyst, 30% activity; 3, used catalyst after oxydative regeneration.

covered by predominantly aliphatic carbon. Since carbon and, especially, nitrogen were detectable in deeper layers as well, a partial blocking of the pore system may be assumed, which was completely reversible by a simple oxydative regeneration treatment. The enrichment of N inside the pore system and the measured XPS N 1s binding energies may be explained by the deposition of linear polymeric species formed by ring-opening reactions of unsaturated nitriles which are preferentially formed inside the zeolite and which are responsible for the deactivation by a pore-blocking mechanism.

The changing $SiO^+/SiOH^+$-SIMS fragment ion profiles indicate varying relative amounts of silanol groups and changes of silanol group distribution gradients in the near-surface regions of the pore system of the zeolite. This finding is evident because of the posttreatment of the B-MFI

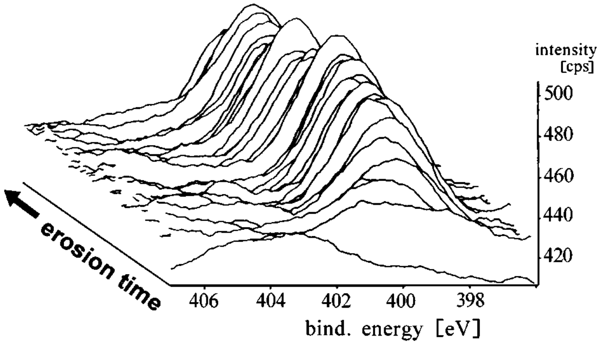

FIG. 4. XPS depth profile of a used B-MFI catalyst, activity 50%; N 1s signal region.

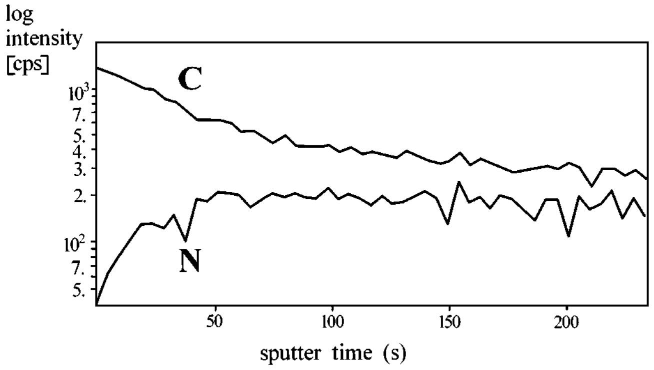

FIG. 5. Used B-MFI catalyst, activity 50%: XPS signal intensities as a function of sputter time. *N.b.*, logarithmic scale.

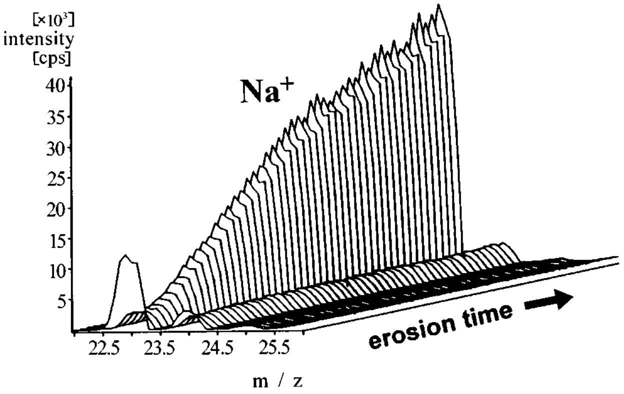

FIG. 6. SIMS depth profile of Na (23) and Mg (24–26), measured on an fresh B-MFI catalyst.

catalyst creating silanol groups and reestablishing nearly the same $SiO^+/SiOH^+$ fragment ion ratio in the topmost atomic layer, as observed for the fresh catalyst. Furthermore, this suggests changes of the surface polarity of the catalyst with increasing service time.

The rather systematic changes of the $SiO^+/SiOH^+$ ratios (Fig. 2) relative to the element ion signals of Si and B (Fig. 1) suggest that, quite surprisingly, realistic and at least qualitative information was obtained in these depth profiling experiments on these porous materials. A decreasing relative intensity of the $SiOH^+$ signal as a function of the time of erosion (Fig. 2) appears to be a suitable indicator that the surface regions are mostly removed and that the analysis proceeds into the inner regions of the material (Figs. 3 and 4). It follows that the $SiOH^+$ profiles of the used catalysts measured by means of SIMS (Fig. 2) and, furthermore, the carbon and the nitrogen profiles which were obtained by means of XPS (Figs. 3–5) represent chemical modifications inside the pore structure of the zeolites.

A pronounced and irreversible deboration effect in the surface regions of the zeolite as a reason for catalyst deactivation was not observed. After removing the carbon layers by an oxydative treatment the shape of a rather constant boron profile was reestablished (Fig. 1). The B level was only slightly affected (Table 2). This is astonishing after a regeneration procedure with oxygen at 500°C for several hours. This result demonstrates that the B-MFI catalyst as prepared loses only a small quantity of boron but afterwards the boron content remains rather constant.

During the use of the zeolite in the catalytic process changes of the Ca and K profiles relative to the Si profile in the near-surface regions of the zeolite were observed, whereas the Na profiles remained largely unchanged. This suggests that Na is located on lattice sites, whereas the Ca is able to diffuse inside the pore system.

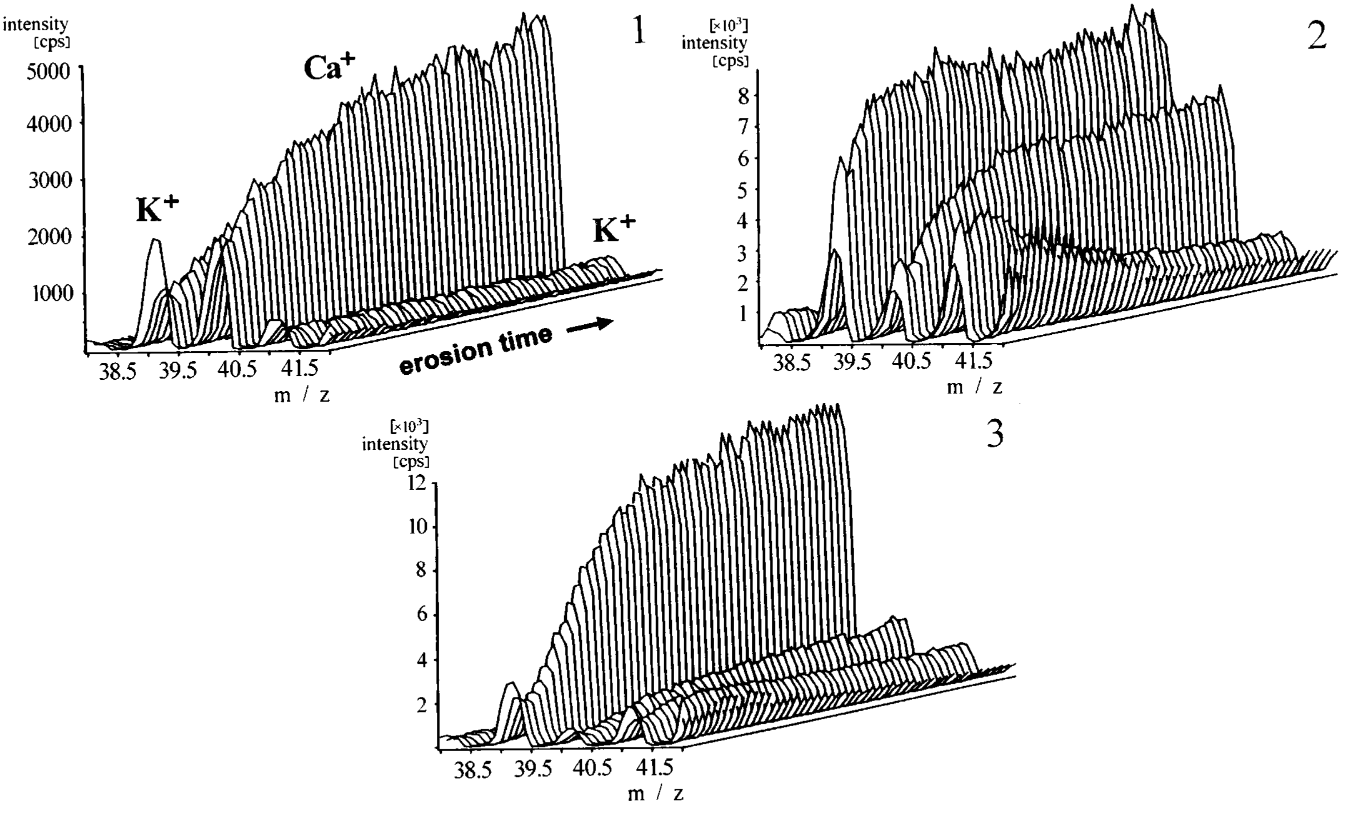

FIG. 7. SIMS depth profile of K (39–41) and Ca (main peak at 40): 1, fresh catalyst; 2, used catalyst, 98% activity; 3, used catalyst, 30% activity.

SIMS and XPS depth profiling measurements are suitable to reveal the chemical modifications in the surface and selvedge regions of porous, oxidic materials. Qualitative interpretations of combined XPS and SIMS data appear to be justified but additional experimental work is required to allow for a more quantitative evaluation of the intensity gradients in the SIMS fragmentation profiles.

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